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Interactions between Organic Compounds and Ionic Liquids. Selectivity and Capacity Characteristics of Ionic Liquids

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1. Introduction

Nowadays, environmental protection is one of the most important matter of concerns. In the last century, chemical engineering industry developed processes involving unit operation using volatile organic components (VOC). Solvents comprise 2/3 of all industrial emissions and 1/3 of all VOC emissions nationwide. Many factories also produce long-lasting gases that do not occur naturally, yet contribute significantly to the enhanced greenhouse effect and global warming that is currently under way. The new constraints facing chemical engineers are to continue to provide society with the products necessary for sustaining a high standard of living, while, at the same time, significantly reduce the environmental impact of the processes we use to do this. Therefore, the reduction of the use of VOCs is a significant research topic in recent years.

In the last ten years, a new class of compounds has emerged and may become a key ally in helping us meet the twin challenges of efficient and environmentally benign chemical processing. These compounds known as Ionic liquids (ILs) or room temperature ionic liquids (RTILs) have received increased attention from both industrial and academic communities because they have the potential to revolutionize the way we think of and use solvents. Because of the lack of measurable vapor pressure, easy recyclability, and no flammability, ionic liquid solvents are viewed by many as "green" solvents. They are organic salts, whose cations, substituents and anions can be varied at will to change their chemical and physical properties. They can be used to redesign processes in order to reduce or eliminate loss of solvents particularly volatile organic compounds (VOCs) (Letcher, 2007). The growth in development in ionic liquids is not only being driven by their potential as green solvents but also by potential improvement in process economics, chemical reactivity, selectivity, and yield. Nowadays, ILs are emerging as alternative green solvents, in other words, as alternative reaction media for synthesis, catalysis and biocatalysis, but also as electrolytes, lubricants or modifiers of mobile and stationary phases in the separation sciences (Letcher, 2007; Rodgers & Seddon, 2002; Rodgers & Seddon, 2003; Alonso et al., 2008; Cadena et al, 2004).

Ionic liquids have been used in industrial processes for more than a decade and their applications continue to expand. For instance, extractive distillation and liquid-liquid extraction with ionic liquids as separating agent is a novel method for separation of ethanol-

water mixture (Arlt et al, 2001), of thiophene from aliphatic hydrocarbons (Alonso et al, 2008). It is clear that ionic liquids may play an important role since regulations regarding liquid hydrocarbon fuels are continuously requiring sulfur content to be reduced to lower levels. The current specification in Europe and in the USA has defined the maximum sulphur content as less as 50 parts per million in gasoline starting from 2005. This level will be reduced to 10 ppm by the year 2010. Their attractiveness has led to the development of several new commercial processes. For example, BASF's BASIL process uses ionic liquids to remove acids from reaction mixtures. The French Petroleum Institute's process called Difasol also uses ionic liquids as reaction solvents for dimerizing butene to octenes. Many new areas of application in the petroleum, chemical and allied industries are emerging for ionic liquids.

The knowledge of the physico-chemical properties of ionic liquids is of great importance. Indeed, a large thermodynamic databank will give a better understanding of the behaviour of ILs in mixtures depending on the ionic structures and the intermolecular interactions. Furthermore, measurement of physical properties for these substances is essential to evaluate the actual potential of an IL as solvent for a particular application. While data on activity coefficients, vapor-liquid equilibria and liquid-liquid equilibria are now available for a number of binary and a few ternary systems, the situation is still not satisfying with respect to a systematic knowledge of these properties and further research work have to fill the remaining gaps. In the beginning of 2000, the majority of research works were focussed on organic synthesis of ILs and on the study of chemical reactions in ILs. Systematic investigations of thermodynamic properties of pure ILs and their mixtures with organic compounds or gases are not always performed. Nevertheless, data for these properties are of considerable importance for selecting appropriate ILs in different applications of chemical engineering.

In this article, we present a general behaviour of organic compounds with ionic liquids using thermodynamic properties such as partition coefficients or activity coefficients at infinite dilution determined using inverse gas chromatography. Infinite dilution activity coefficients (γ^∞) are very useful for process synthesis and design. For example, activity coefficients at infinite dilution can be directly used for the selection of solvents for azeotropic/extractive distillation, liquid extraction, solvent-aided crystallization, and even chemical reaction. Activity coefficients at infinite dilution γ^∞ give a direct measure of interactions between unlike molecules in the absence of solute-solute interactions. With others respects, numerous approaches may be used to characterize the interactions between the solute and the ionic liquids. Using chromatographic data, we propose to characterize solute-ionic liquids interactions using a solvation model. Then, the last part will be devoted to a brief presentation of the influence of structure of ionic liquid on selectivity and capacity for four separation problems.

2. Solvation models used in gas chromatography

2.1 Linear solvation energy relationship

In numerous solvation models, the partition of a solute between the gas phase and a solvent (or stationary phase) may be described by a cavity theory of solution (Vitha & Carr, 2006; Abraham et al., 1999) in which the solvation process is divided into three steps. In the step 1, a cavity of suitable size to accommodate the solute is created in the solvent (Figure 1). This process is endoergic because work is required to disrupt solvent-solvent interactions. In the

second step, the solvent molecules around the cavity are reorganized from their original positions to the positions they will adopt when the solute is in equilibrium with the solvent. Of course, these positions are not fixed but are averages of solvent positions. The Gibbs energy change for such reorganization is assumed to be negligible, by analogy with the melting of a solid. However, enthalpy and entropy changes in reorganizations may be large, again by analogy with the melting of a solid. In the last step, the solute is introduced into the reorganized cavity, and various solute-solvent interactions are set up, all of which are exoergic.

Several thermodynamic properties are related to partitioning between water and other phases, for example octanol (K_{ow}) or the pure compound itself (water solubility). These partitioning processes can be understood from thermodynamic concepts—like free energy, chemical potential and fugacity. The equilibrium partition constant between two phases, on a mole fraction basis, can be expressed as:

$$K_{12} = \exp(-\Delta_{12}G_i/RT) \quad (1)$$

where $\Delta_{12}G_i$ is the Gibbs energy (or free energy) of transfer between the two phases, R is the general gas constant and T is the absolute temperature. The Gibbs energy sums up both the enthalpic ($\Delta_{12}H$) and entropic ($\Delta_{12}S$) effects resulting from changes in intermolecular interactions:

$$\Delta_{12}G_i = \Delta_{12}H_i - T \Delta_{12}S_i \quad (2)$$

The calculation of partitioning from structural or other descriptors therefore requires the modelling of these effects. The Gibbs energy change can also be separated into the contributions of van der Waals and polar interactions, assuming that these are additive:

$$\Delta_{12}G_i = \Delta_{12}G_i^{vdW} + \Delta_{12}G_i^{polar} \quad (3)$$

In the early 1980's, (Taft & Kamlet, 1976; Kamlet et al., 1977; Kamlet et al., 1983; Kamlet & Taft, 1985; Kamlet et al., 1988) have developed the basic concept of linear solvation energy relationships (LSERs). They have demonstrated for thousands of chemical systems that some property which is linearly related to either a free energy of reaction, a free energy of transfer, or an activation energy can be correlated with various fundamental molecular properties of the solvents or solutes involved. Chromatographic retention and in particular logarithmic retention factors ($\log k'$), logarithmic partition coefficients ($\log K_L$) are linear free energy parameters and as such one can linearly correlate these data with the molecular properties of the solutes using the LSER model (Abraham & Whiting, 1992; Abraham et al., 1993a; Park & Carr, 1989; Weckwerth & Carr, 1998).

The most recent representation of the LSER model proposed by (Abraham et al., 1987; Abraham et al., 1990, Abraham et al., 1991, Abraham et al., 1993b) is given by equation (4)

$$\log SP = c + eE + sS + aA + bB + lL \quad (4)$$

Where SP is a solvation parameter related with the free energy change such as gas-liquid partition coefficient, specific retention volume or adjusted retention time at a given temperature. The capital letters represent the solutes properties and the lower case letters the complementary properties of the ionic liquids. The solute descriptors are the excess molar refraction E , dipolarity/ polarizability S , hydrogen bond acidity basicity, A and B , respectively, and the gas-liquid partition coefficient on *n*-hexadecane at 298 K, L . The solute

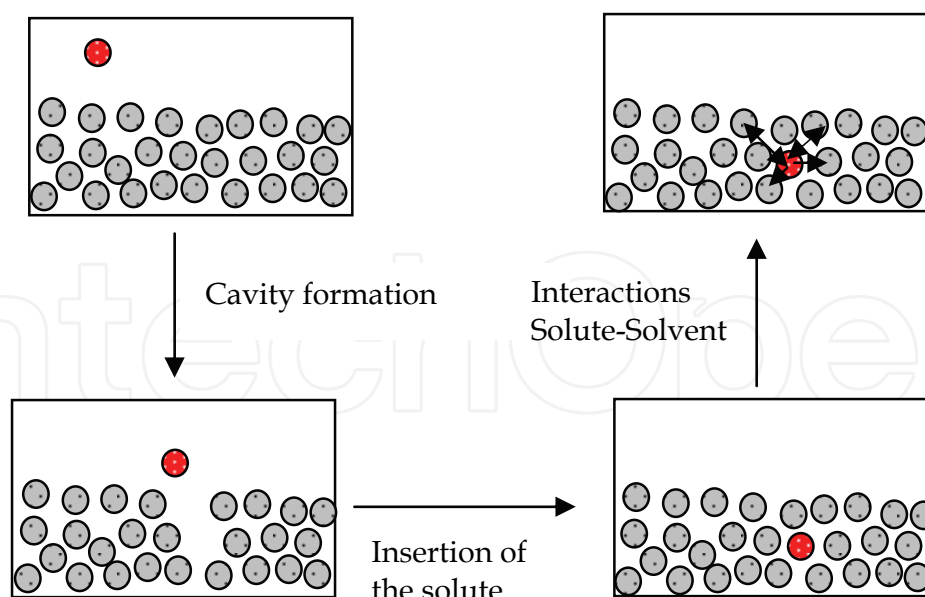


Fig. 1. Model of the solvation process.

descriptors may be determined using inverse gas chromatography or estimated using a group contribution method. A databank of descriptors for about 3000 compounds may be found in the literature (Platts et al., 1999, Abraham & Platts, 2001, Mutelet & Rogalski, 2001). The coefficients c , e , s , a , b and l are not simply fitting coefficients, but they reflect complementary properties of the solvent phase. These coefficients are determined by multiple linear regression of equation (4). This model was strongly applied to characterize chemicals products, petroleum fluids.

3.2 Application of linear solvation energy relationship on ionic liquids

In the literature, there is a large amount of data of partition coefficients or activity coefficients measured by gas-liquid chromatography or by dilutor technique. Some system constants for various ionic liquids and classical solvents at 25 °C are summarized in Table 1. The data for the 1-ethanol-3-methylimidazolium tetrafluoroborate, 1-ethanol-3-methylimidazolium hexafluorophosphate, 1,3-dimethylimidazolium dimethylphosphate and 1-ethyl-3-methylimidazolium diethylphosphate (Revelli et al., 2009a), 1-Butyl-3-methylimidazolium tetrafluoroborate (Revelli et al., 2009b), n-Acryloyloxypropyl-N-methylimidazolium bromide and n-Methacryloyloxyhexyl-N-methylimidazolium bromide (Mutelet et al., 2008), 1-Propenyl-3-alkyl-imidazolium bromide (Mutelet et al., 2006), 1-butyl-3-methylimidazolium octyl sulfate and 1-ethyl-3-methylimidazolium tosylate (Mutelet & Jaubert, 2006), Triethylsulphonium bis(trifluoromethylsulfonyl)imide (Domańska & Marciniak, 2009a), 1-Methyl-3-ethylimidazolium bis(trifluorosulfonyl)-amide and 1,2-Dimethyl-3-ethylimidazolium bis(trifluorosulfonyl)-amide (Krummen et al., 2002) were taken from the sources indicated. (Poole & Poole, 2010) found that the system constants of LSER model for the room temperature ionic liquids fall into the range $e = -0.62$ to 0.86 , $s = 1.7$ – 2.8 , $a = 2.1$ – 7.3 , $b = 0$ – 1.07 , and $l = 0.35$ – 0.96 . Compared with the scale of the polar organic solvents $e = -0.60$ to 0.82 , $s = 0.54$ – 2.8 , $a = 0.28$ – 5.50 , $b = 0$ – 4.8 , and $l = -0.21$ to 0.98 , we can see that both scales are similar indicating that the solvation properties for the room temperature ionic liquids are classical and fit quite well into the scales developed for polar molecular solvents.

Ionic liquids	System constants					
	e	s	a	b	l	c
1-ethanol-3-methylimidazolium hexafluorophosphate	0	3.03	2.89	1.13	0.47	-1.14
1-ethanol-3-methylimidazolium tetrafluoroborate	0	3.03	3.64	0.763	0.5	-1.35
1,3-dimethylimidazolium dimethylphosphate	0.86	2.59	7.27	0	0.35	-0.61
1-ethyl-3-methylimidazolium diethylphosphate	0.26	1.97	6.9	0	0.54	-0.09
1-Butyl-3-methylimidazolium tetrafluoroborate	0.56	2.82	3.27	0.48	0.5	-0.77
n-Acryloyloxypropyl-N-methylimidazolium bromide	0	2.88	5.5	0	0.48	-1.03
n-Methacryloyloxyhexyl-N-methylimidazolium bromide	0	2.46	5.36	0	0.57	-0.87
1-Propenyl-3-methyl-imidazolium bromide	0	2.16	5.19	0	0.53	-1.86
1-Propenyl-3-octyl-imidazolium bromide	0	1.72	4.96	0	0.57	-1.6
1-Propenyl-3-decyl-imidazolium bromide	0	1.73	4.89	0	0.66	-1.58
1-Propenyl-3-dodecyl-imidazolium bromide	0	1.44	4.87	0	0.72	-1.51
1-Butyl-3-methylimidazolium octyl sulfate	0	1.47	4.05	0	0.68	-0.237
1-Ethyl-3-methylimidazolium tosylate	0.54	2.4	4.81	0.17	0.48	-0.84
n-Butylammonium thiocyanate	0.14	1.65	2.76	1.32	0.45	-0.75
1-Methyl-3-ethylimidazolium bis(trifluorosulfonyl)-amide	0.148	2.277	2.172	1.041	0.629	-0.439
1.2-Dimethyl-3-ethylimidazolium bis(trifluorosulfonyl)-amide	0.214	2.347	2.075	0.896	0.655	-0.565
Triethylsulphonium bis(trifluoromethylsulfonyl)imide	0.114	2.37	2.34	0.696	0.642	-0.803
1-Ethyl-3-methylimidazolium Trifluoroacetate	0.608	1.63	4.21	1.81	0.584	-0.918
1-Butyl-3-methylimidazolium Trifluoromethanesulfonate	0.399	2.03	3.49	0.681	0.647	-0.784
Organic solvents						
Trifluoroethanol	-0.547	1.339	2.213	3.807	0.645	-0.092
Methanol	-0.22	1.17	3.7	1.43	0.769	-1.27
Water	0.82	2.74	3.9	4.81	-0.213	0
1,2 Dichloroethane	-0.47	1.676	0.92	0.486	0.927	0.025
Dry methyl acetate	-0.447	1.675	2.625	0.213	0.874	0.129
Dry ethyl acetate	-0.352	1.316	2.891	0	0.916	0.182
Ethylene glycol	0.217	1.427	4.474	2.687	0.568	-0.898
Benzene	-0.313	1.053	0.457	0.169	1.02	0.107
2-(Cyclohexylamino)ethanesulfonate	0.07	1.57	3.67	0	0.51	-0.83

Table 1. LSER descriptors of ionic liquids and classical solvents determined at 313.15 K.

The ($c + IL$) term gives information on the effect of cohesion of the ionic liquids on solute transfer from the gas phase. In general, the ionic liquids are cohesive solvents; they interact weakly via nonbonding and π -electrons (r system constant is zero) and are not much different to other polar non-ionic liquids. The ionic liquids are roughly as dipolar/polarizable as classical solvents. The hydrogen-bond basicity of the ionic liquid (a system constants) are considerably larger than values obtained for non ionic phases (0-2.1) (Poole, 2004). The hydrogen-bond basicity of ILs depends on the anion grafted on the cation. ILs can be slightly more hydrogen-bond basic than dimethyl sulfoxide and *N*-methylpyrrolidinone, and are weak to moderate hydrogen-bond acids, similar to the aliphatic alcohols. From Table 1 and data collected by (Poole & Poole, 2010), we can see that the hydrogen-bond acidity of the ionic liquids depends largely on the cation and is lower for the 1,3-dialkylimidazolium salts with an alkyl group at C-2 position than 1,3-dialkylimidazolium salts.

3.1 Predictive models based on LSER model coupled to a group contribution method

In order to quantify intermolecular solute-IL interactions, (Abraham et al., 2003; Acree & Abraham, 2006) reported mathematical correlations based on the general Abraham solvation parameter model for the gas-to-solvent, K_L , and water-to-solvent, P , partition coefficients. Recently, (Sprunger et al., 2007; Sprunger et al., 2008; Sprunger et al., 2009a; Sprunger et al., 2009b) modified the Abraham solvation parameter model:

$$\begin{aligned} \text{Log } K_L = & c_{\text{cation}} + c_{\text{anion}} + (e_{\text{cation}} + e_{\text{anion}}) \cdot E + (s_{\text{cation}} + s_{\text{anion}}) \cdot S + (a_{\text{cation}} + a_{\text{anion}}) \cdot A \\ & + (b_{\text{cation}} + b_{\text{anion}}) \cdot B + (l_{\text{cation}} + l_{\text{anion}}) \cdot L \end{aligned} \quad (5)$$

$$\begin{aligned} \text{Log } P = & c'_{\text{cation}} + c'_{\text{anion}} + (e'_{\text{cation}} + e'_{\text{anion}}) \cdot E + (s'_{\text{cation}} + s'_{\text{anion}}) \cdot S + (a'_{\text{cation}} + a'_{\text{anion}}) \cdot A \\ & + (b'_{\text{cation}} + b'_{\text{anion}}) \cdot B + (v_{\text{cation}} + v_{\text{anion}}) \cdot V \end{aligned} \quad (6)$$

by rewriting each of the six solvent equation coefficients as a summation of their respective cation and anion contribution. The dependent variables in eqs 5 and 6 are solutes descriptors as follows: **E** and **S** refer to the excess molar refraction in units of (cm³.mol⁻¹)/10 and dipolarity/polarizability descriptors of the solute, respectively, **A** and **B** are measures of the solute hydrogen-bond acidity and basicity, **V** is the McGowan volume in units of (cm³.mol⁻¹)/100 and **L** is the logarithm of the gas-to-hexadecane partition coefficient at 298 K. Sprunger et al. calculated equation coefficients for 8 cations and 4 anions using a database that contained 584 experimental log K_L and 571 experimental log P values. No loss in predictive accuracy was observed by separating the equation coefficients into individual cation-specific and anion-specific values. The major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more ILs. In Sprunger's approach, the major advantage of splitting the equation coefficients into individual cation-specific and anion-specific contributions is that one can make predictions for more ILs. Most of the cations are alkyylimidazolium. The use of this model is somewhat limited since it can not be extrapolated to alkyylimidazolium ionic liquids not initially defined by the method (e.g. with long alkyl chains).

In the development of (Revelli et al, 2010a), the cation with its alkyl chains is splitted in different contributions: (CH₃, CH₂, N, CH_{cyclic}...). The approach allows to have a predictive model. The aim of this work was to develop a group contribution method allowing to estimate the log K_L and Log P of organic compounds in ionic liquids at 298 K. Using the LSER model proposed by Abraham, the group contribution method expresses LSER coefficients c_i , e_i , s_i , a_i , b_i and l_i of equation (7) or c'_i , e'_i , s'_i , a'_i , b'_i and v_i of equation (8) by:

$$\text{Log} K_L = \sum_i^{21} n_i \times c_i + \sum_i^{21} n_i \times e_i \cdot E + \sum_i^{21} n_i \times s_i \cdot S + \sum_i^{21} n_i \times a_i \cdot A + \sum_i^{21} n_i \times b_i \cdot B + \sum_i^{21} n_i \times l_i \cdot L \quad (7)$$

$$\text{Log} P = \sum_i^{21} n_i \times c'_i + \sum_i^{21} n_i \times e'_i \cdot E + \sum_i^{21} n_i \times s'_i \cdot S + \sum_i^{21} n_i \times a'_i \cdot A + \sum_i^{21} n_i \times b'_i \cdot B + \sum_i^{21} n_i \times v_i \cdot V \quad (8)$$

Where n_i is the number of group i present in the ionic liquid.

The experimental data used to calculate Abraham's model ion-specific equation coefficients were taken from the collection of (Sprunger et al., 2007; Sprunger et al., 2008; Sprunger et al., 2009a; Sprunger et al., 2009b) and were updated with recent data (Revelli et al., 2010a). A total of 1450 gas-liquid partition coefficients and 1410 water-to-liquid partition coefficients were used for the calculation. Solutes were mainly n-alkanes, cycloalkanes, alkenes, alkynes, aromatics, alcohols, ethers, aldehydes, ketones, chloroalkanes. The E -scale varies from 0 to 1.5, the S -scale from 0 to 1.72, the A -scale from 0 to 1.04, the B -scale from 0 to 1.28, the L -scale from -1.200 to 7.833 and the V -scale from 0.109 to 1.799. The dataset is composed of 27 imidazolium based ionic liquids, 3 ammonium, 3 pyridinium and 4 pyrrolidinium based ionic liquids. The authors also add sulphonium and phosphonium ionic liquids although only one set of K_L (or P) data may be found for these families. The twenty one groups which are defined in this method are listed in Table 2. The decomposition into groups of the ionic liquids is very easy, that is as simple as possible. No substitution effects are considered. No exceptions are defined. In Figure 2 are represented all ionic liquids studied in this work. Five groups are defined to describe the chains R_1 , R_2 , R_3 and R_4 grafted on the cation: CH₃, CH₂, -O-, -O-N_{cycl} and -OH. These groups allow the calculation of partition coefficients of alkyl based ionic liquids but also functionalized ionic liquids such as ether, alcohols. The remaining seven groups are: CH_{2cyclic}, CH_{cyclic}, C_{cyclic}, N_{cyclic}, N⁺ (ammonium cation), P⁺ (phosphonium cation) and S⁺ (sulphonium cation).

More precisely, N_{cyclic} represents two structures: $-N^+$ and $-N-$. Nine groups are used

for anions: bis(trifluoromethylsulfonyl)imide: $(TF)_2 N^-$, hexafluorophosphate: PF_6^- , tetrafluoroborate: BF_4^- , ethylsulfate: $EtSO_4^-$, octylsulfate: $OcSO_4^-$, thiocyanate: SCN^- , trifluoromethylsulfonate: $CF_3SO_3^-$, trifluoroacetate: ACF_3^- and dicyanamide: $(CN)_2 N^-$. As an example, let's have a look at the decomposition of 1-butyl-3-methylimidazolium hexafluorophosphate. In this case, the decomposition of the molecule into elementary groups is: 2 groups 1 (-CH₃) + 3 groups 2 (-CH₂) + 3 groups 7 (C_{cyclic}) + 2 groups 9 (N_{cyclic}) + 1 group 14 (PF₆⁻).

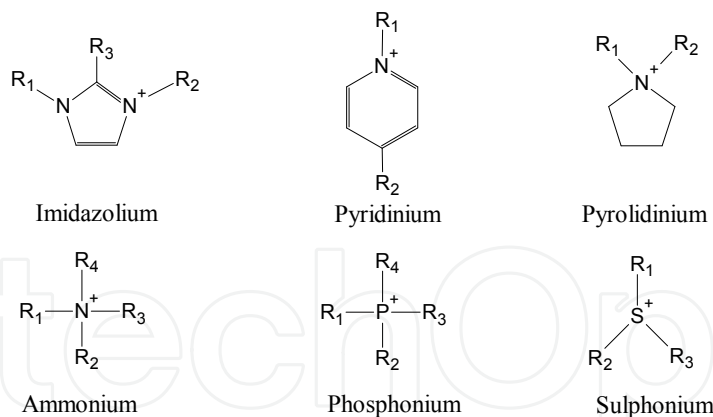


Fig. 2. Cation of six families of ionic liquids.

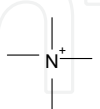
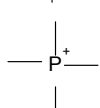
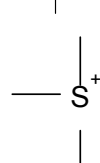
Cation's group	Definition	Anion's group	Definition
Group 1 CH ₃ -	CH ₃ from alkyl chain R ₁ , R ₂ ,R ₃ or R ₄	Group 13 (TF) ₂ N ⁻	bis(trifluoromethyl sulfonyl)imide
Group 2 -CH ₂ -	CH ₂ from alkyl chain R ₁ , R ₂ ,R ₃ or R ₄	Group 14 PF ₆ ⁻	hexafluorophosphate
Group 3 -O-	-O- in alkyl chain R ₁ , R ₂ ,R ₃ or R ₄	Group 15 BF ₄ ⁻	tetrafluoroborate
Group 4 -O-N _{cyclic} -	Oxygenated atom connected directly to N _{cyclic}	Group 16 EtSO ₄ ⁻	Ethylsulfate
Group 5 -OH	-OH from alkyl chain R ₁ , R ₂ ,R ₃ or R ₄	Group 17 OcSO ₄ ⁻	Octylsulfate
Group 6 CH ₂ _{cyclic}	CH ₂ cyclic in pyrolidinium's cation	Group 18 SCN ⁻	Thiocyanate
Group 7 CH _{cyclic}	CH cyclic in imidazolium or pyridinium's cation	Group 19 CF ₃ SO ₃ ⁻	trifluoromethylsulfonate
Group 8 C _{cyclic}	C cyclic in imidazolium or pyridinium's cation	Group 20 ACF ₃ ⁻	trifluoroacetate
Group 9 N _{cyclic}	Cyclic nitrogen (imidazolium, pyridinium and pyrolidinium) Ammonium's cation	Group 21 (CN) ₂ N ⁻	dicyanamide
Group 10 			
Group 11 	Phosphonium's cation		
Group 12 	Sulphonium's cation		

Table 2. Description of the 21 groups used for the estimation of LogK_L and LogP

Group contribution model coupled to LSER (GC-LSER) for estimating the gas-to-ionic liquids partition coefficients and water-to-ionic liquids partition coefficients allows to predict with good accuracy $\text{Log } K_L$ and $\text{Log } P$ at 298 K of not only alkyl based ionic liquids but also functionalized ionic liquids. The parameters of the group contribution methods were determined for imidazolium, pyridinium, pyrrolidinium, phosphonium, ammonium and sulphonium based ionic liquids containing several different anions. A comparison between the experimental and calculated values showed that the proposed models describe the experimental data available with a mean absolute error of about 0.15 log unit. The predictive power of the model was appreciated with three ionic liquids not taken into account in the database, 1-ethyl-3-methylimidazolium trifluoromethylsulfonate (Olivier et al., 2010), 1-hexadecyl-3-methylimidazolium tetrafluoroborate (Mutelet & Jaubert, 2007) and 1-ethanol-3-methylimidazolium hexafluorophosphate (Revelli et al., 2009a). This training set composed of 130 $\text{log } K_L$ and 126 $\text{log } P$ is estimated with a mean absolute error on $\text{Log } K_L$ and $\text{Log } P$ of about respectively, 0.15 and 0.19. A study of results indicated that light hydrocarbons showed larger deviations. In the case of data coming from inverse gas chromatography, it is well known that light hydrocarbons are prime to adsorption. If retention data are not corrected from this adsorption, partition coefficient may be over or underestimated. Plots of calculated values of $\text{Log } K_L$ of solutes in 1-butyl-4-methylpyridinium thiocyanate and in 1-butyl-1-methylpyrrolidinium thiocyanate based on equation 7 against the measured values by (Domańska and Krolikowska, 2010) are presented in Figure 3. While the model is probably somewhat limited in prediction for pyridinium and pyrrolidinium based ionic liquids because of the poor dataset for these cations, results obtained are satisfactory.

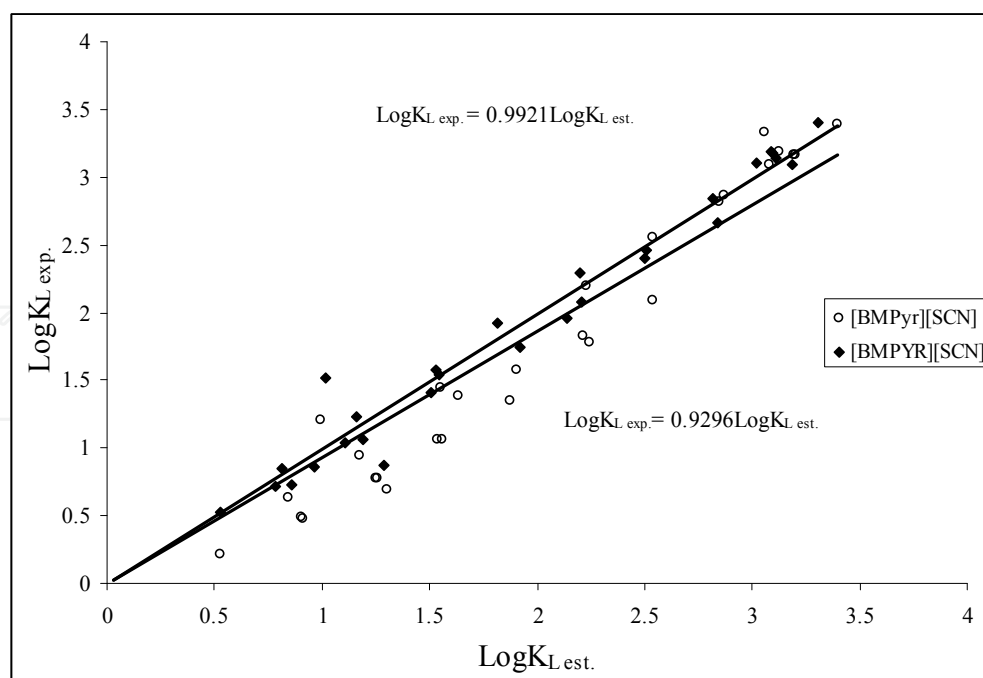


Fig. 3. Prediction of $\text{Log } K_L$ at 298.15 K of organic compounds in two ionic liquids using the GC-LSER. 1-butyl-4-methylpyridinium thiocyanate [BMPyr][SCN] and 1-butyl-1-methylpyrrolidinium thiocyanate [BMPYR][SCN].

3. General behaviour of ionic liquids with organic compounds.

The large dataset of partition coefficients (or activity coefficients at infinite dilution) published in the literature may be used to present a general behaviour of solutes in ionic liquids. The values of activity coefficients at infinite dilution (γ^∞) for the *n*-alkanes increase with an increase in carbon number. In most ionic liquids, the high γ^∞ values observed with *n*-alkanes indicate their low solubility in ionic liquids. The γ^∞ values of *n*-alkanes are higher than the values obtained with cyclohexane, alkenes, alkynes and aromatics. Introduction of a double or triple bond in the *n*-alkanes decreases the γ^∞ values.

Cyclization of the alkane skeleton reduces the value of γ^∞ in comparison to that of the corresponding linear alkanes (e.g., hexane). Aromatics with their π -delocalized electrons have smaller γ^∞ values, presumably because of the interaction with the cation species. Using computer simulation, (Lynden-Bell et al., 2007) showed that the cations are found to interact predominantly with the ring of the benzene while the anions interact with the ring hydrogens to a first approximation.

In the series of chloromethanes, it is usually observed that γ^∞ values strongly increase from dichloromethane to tetrachloromethane. This behavior observed with all types of ionic liquids indicates that polar compounds have better solubility in the ILs when attractive interaction between polar molecules and the charged ions of the solvent is possible. The γ^∞ values for the alcohols are relatively small (ranging between 1.2 and 4.6). The lone pair of electrons on the oxygen atom could interact with the ionic liquid cation, and the acidic proton is attracted by oxygen atoms in the cation. γ^∞ values of branched alkanol skeleton are smaller than γ^∞ values of the corresponding linear alcohol. γ^∞ values of *n*-alkanols increase with increasing chain length. γ^∞ values of ethers and amine are higher in comparison with those of the alcohols. For most solutes, their solubility increases when the alkyl chain length grafted on the ionic liquid increases. The behavior of solutes with ionic liquids is also strongly affected by the nature of the chain grafted on the ionic liquids. For example, grafting a polar chain on the cation of dicyanamide based ionic liquid increases strongly the interactions. Replacing the 1-ethyl-3-methylimidazolium cation by 1-(3-cyanopropyl)-3-methylimidazolium in dicyanamide based ionic liquids, the activity coefficients values of *n*-hexane are divided by two (241 to 111).

The alkoxymethyl-group grafted on the imidazolium cation makes the ionic liquid more polar and with the possible anti-microbial activities (Pernak et al., 2001). (Domańska, A. Marciniak, 2009b) studied the interaction between organic compounds and 1-hexyloxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide and 1,3-dihexyloxymethyl-imidazolium bis(trifluoromethylsulfonyl)-imide. The authors found that ILs with two alkoxymethyl groups in the cation reveals stronger interactions with solutes, e.g. additional interaction of the IL with *n*-alkanes, alkenes and alkynes (i.e. Van der Waals interaction between alkane chains of the solute and the cation), and also stronger interaction with aromatic hydrocarbons, thiophene and alcohols (hydrogen bonding, n - π , or π - π interactions).

(Revelli et al, 2009c) measured activity coefficients at infinite dilution of organic compounds in the ionic liquid trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl)imide. As observed with imidazolium-based ionic liquids, cations with a long alkyl chain tend to increase the solubility of most organic compounds in IL. The activity coefficients of 39 organic compounds in this IL are below unity apart from the alkanes and alcohols indicating a strong affinity of the solutes for the ionic liquid. The introduction of a cyanoalkyl chain dramatically decreases the solubility of apolar compounds in ILs. Aromatics, alkenes and

alkynes have lower interactions with cyanoalkylimidazolium based ILs than dialkylimidazolium. There is a lack of information concerning piperidinium based ionic liquids. In their recent study, (Domańska & Paduszyński, 2010a) demonstrate that 1-propyl-1-methylpiperidinium bis{(trifluoromethyl)sulfonyl}imide behaves like the other measured ionic liquids based on different cations.

4. Selectivity and capacity of ionic liquids

From the data of activity coefficients at infinite dilution, selectivities S_{12}^{∞} and capacities k_1^{∞} at infinite dilution may be estimated using the classical equations (9) and (10):

$$S_{12}^{\infty} = \frac{\gamma_{1/RTIL}^{\infty}}{\gamma_{2/RTIL}^{\infty}} \quad (9)$$

$$k_1^{\infty} = \frac{1}{\gamma_{1/RTIL}^{\infty}} \quad (10)$$

In figure 4, the influence of the anion on the selectivity is presented for the separation of {benzene/hexane} using 1-ethyl-3-methylimidazolium based ionic liquids. The highest selectivity is obtained with the thiocyanate anion followed by tetrafluoroborate and tosylate anions. The increasing of the fluor atoms number on fluorinated anions decreases the selectivity of ionic liquids. In the family of fluorinated anions, hydrocarbons have a better affinity with anions containing the lowest fluor atoms number. The solubility of nopolar compounds increases with an increasing of the alkyl chain length grafted on the cation. This means that the selectivity of separation of organic compounds in binary systems {organic compounds + aliphatics} decreases when the alkyl chain length of the IL increases (Figure 5). The influence of the anion for 1-ethyl-3-methylimidazolium based ionic liquids on the

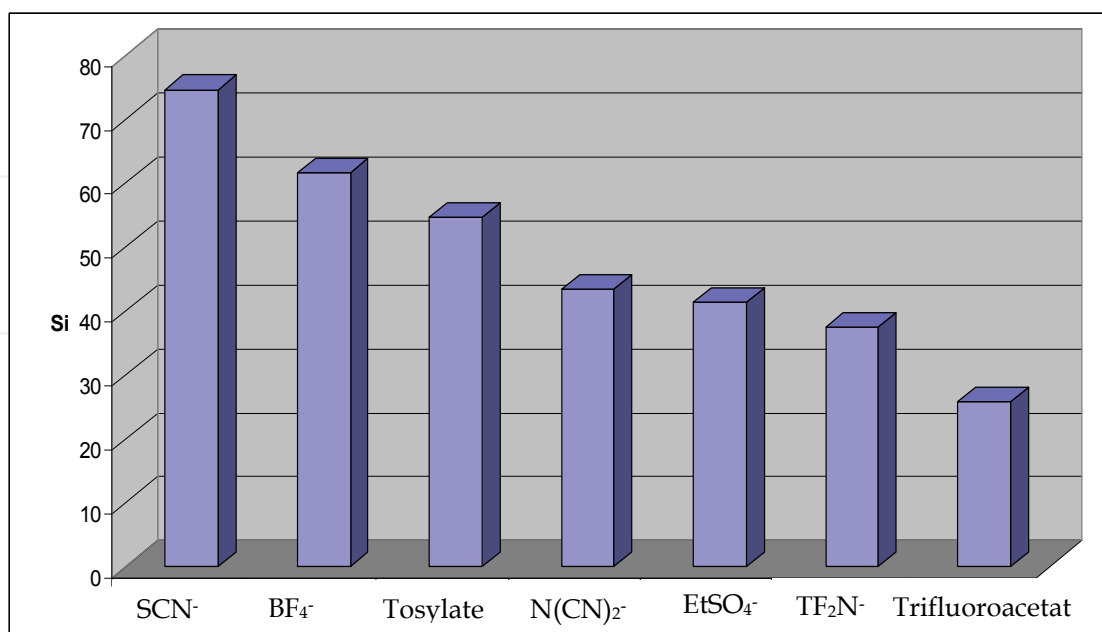


Fig. 4. Influence of the anion on the separation of {benzene-hexane} using 1-ethyl-3-methylimidazolium based ionic liquids at 323.15K.

capacity k_1^∞ is represented in figure 6. The best capacity is obtained for $[\text{TF}_2\text{N}]$ anion and is close to classical solvents used in the industry. Changing $[\text{TF}_2\text{N}]$ anion by dicyanamide or tosylate or trifluoromethanesulfonate anions divides by two the capacity of the corresponding ionic liquid. (Marciniak, 2010) analysed the influence of the cation and anion structures of the ionic liquid but also the effect of the temperature on the selectivity and the capacity for aliphatics/aromatics and n-hexane/hex-1-ene separation problems. The author showed that the highest values of selectivity is observed with ionic liquids containing small alkyl chains, e.g. based on the following cations $[\text{mmim}]^+$, $[\text{emim}]^+$, $[\text{ePY}]^+$, $[\text{Et}_3\text{S}]^+$ coupled to a thiocyanate group in the structure. Unfortunately, when the ionic liquid reveals high values of the selectivity, the capacity always takes low values.

Selectivities S_{12}^∞ and capacities k_1^∞ are listed in Table 3 for four separation problems: hexane/benzene, hexane/methanol, hexane/thiophene, cyclohexane/thiophene for ILs at $T = 323.15$ K. The selectivities and capacities were calculated using experimental activity coefficient at infinite dilution in 1-ethanol-3-methylimidazolium bis((trifluoromethyl)-imide, 1,3-dimethoxyimidazolium bis((trifluoromethyl)sulfonyl)imide, 1-(methylethylether)-3-methylimidazolium bis((trifluoromethyl)sulfonyl)sulfonyl)imide and 1-(3-cyanopropyl)-3-methylimidazolium dicyanamide, (Revelli et al., 2010b), 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Deenadayalu et al., 2005), 1-hexyloxymethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)-imide and 1,3-dihexyloxymethyl-imidazolium bis(trifluoromethylsulfonyl)-imide (Domańska & Marciniak, 2009b), 4-methyl-N-butylpyridinium bis(trifluoromethylsulfonyl)-imide (Domańska & Marciniak, 2009c), triethylsulphonium bis(trifluoromethylsulfonyl)imide (Domańska & Marciniak, 2009a), 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Heintz et al., 2006), trihexyl(tetradecyl)phosphonium bis(trifluoromethylsulfonyl)imide (Revelli et al., 2009c), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (Krummen et al., 2002), 1-ethyl-3-methylimidazolium dicyanamide and trimethylhexylammonium bis((trifluoromethyl)sulfonyl)amide (Mutelet et al., 2010), 1-ethanol-3-methylimidazolium tetrafluoroborate, 1-ethanol-3-methylimidazolium hexafluorophosphate (Revelli et al., 2009a). Selectivities obtained with $[\text{TF}_2\text{N}]$ based ionic liquids and classical solvent used in industry such as sulfolane (30.5), dimethylsulfoxide (22.7) and n-methylpyrrolidinone (12.5) are of the same order of magnitude. The selectivity of such ionic liquids does not increase by replacing the alkyl chain by an ether chain. Concerning dicyanamide ionic liquids, 1-cyanopropyl-3-methylimidaolium dicyanamide has a relatively high selectivity. The S_{12}^∞ values obtained with dicyanamide based ILs show the possibility of using these ILs as an extractive medium for different separation processes. The selectivity of dicyanamide based ILs for {hexane + methanol} mixture is particularly large compared to the value for classical solvents. Then, $[\text{C}_2\text{OHmim}]$ cation coupled to the $[\text{TF}_2\text{N}]$ anion has a small selectivity.

The temperature is an important parameter on selectivity and capacity. For most problems of separation, the selectivity decreases with an increase of the temperature for all imidazolium based ionic liquids. (Marciniak, 2010) found that the influence of the temperature is more important with cations with short aliphatic chains. Because most of the activity coefficients of solutes in ILs decrease with an increase of temperature, the corresponding capacities increase. The selectivities for the extraction of thiophene from benzene follow a similar trend than the selectivities for the system {hexane/ benzene}. For ionic liquids based on phosphonium and ammonium cations with long alkyl chains, the influence of the temperature is weak.

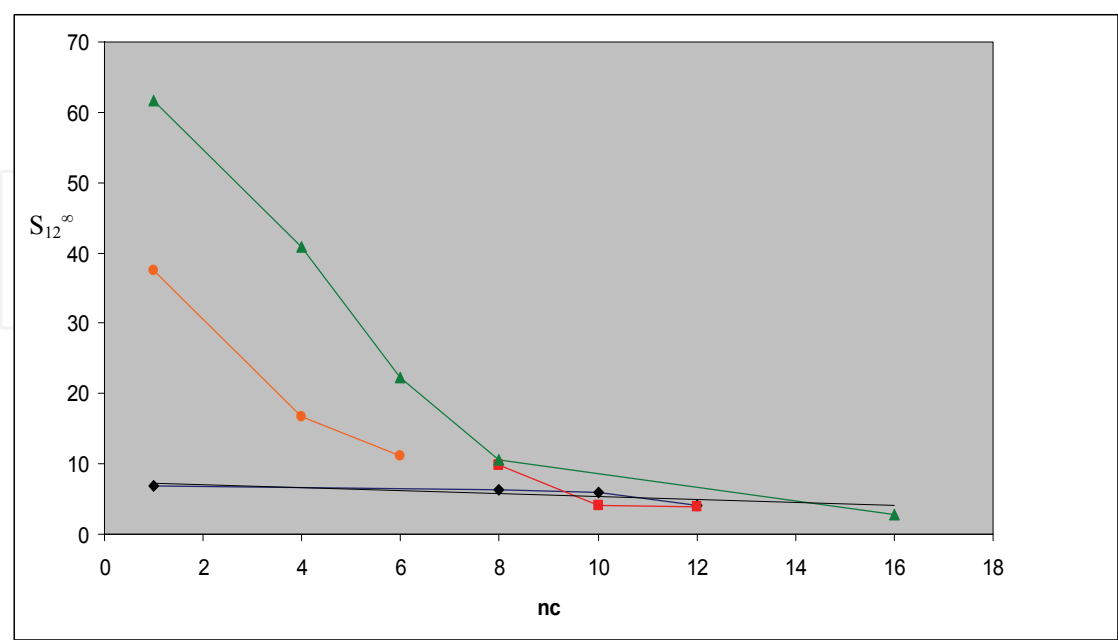


Fig. 5. Influence of the alkyl chain length grafted on the cation on the separation of {benzene-hexane} using : ▲n-alkyl-3-methylimidazolium tétrafluoroborate, ● 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, ■ 1-propyl boronic acid-3-alkyl-imidazolium bromide et ◆ 1-propenyl-3-alkyl-imidazolium bromide.

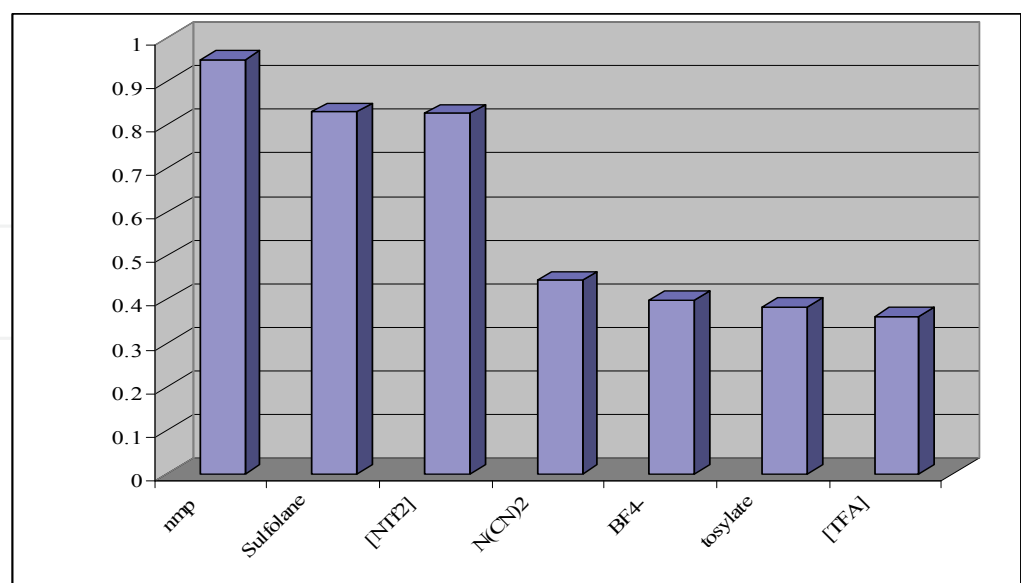


Fig. 6. Influence of the anion on the capacity of {benzene-hexane} using 1-ethyl-3-methylimidazolium based ionic liquids at 323.15 K.

Ionic liquids		$S_{12}^{\infty} / k_1^{\infty}$			
Anion	Cation	Hexane/ Benzene	Hexane/ Methanol	Hexane/ Thiophene	Cyclohexane/ Thiophene
[Tf ₂ N]	1,3-dimethoxyimidazolium	21.3 / 0.47	42.05 / 0.94	24.8 / 0.94	12.6 / 0.94
	1-(methylethylether)-3-methylimidazolium	15.5 / 0.85	17.4 / 0.93	18.1 / 1.0	10.9
	1-ethanol-3-methylimidazolium	20.6 / 0.47	49.1 / 1.12	24.7 / 0.56	14.2 / 0.56
	1-ethyl-3-methylimidazolium	37.5 / 1.43	19.5 / 1.20	-	-
	1-(hexylmethylether)-3-methylimidazolium	9.1 / 1.23	6.8 / 0.91	10.0 / 1.35	6.4 / 1.35
	1,3-di(hexylmethylether)imidazolium	4.9 / 1.67	3.2 / 1.06	5.3 / 1.75	3.7 / 1.75
	1-butyl-3-methylimidazolium	16.7 / 1.11	-	-	-
	1-hexyl-3-methylimidazolium	9.5 / 1.29	6.1 / 0.82	-	-
	trimethylhexylammonium	9.9 / 1.01	8.5 / 0.86	10.7 / 1.09	7.2 / 1.09
	4-methyl-N-butyl-pyridinium	18.8 / 1.43	21.2 / 0.83	10.6 / 1.56	6.1 / 1.56
	triethylsulphonium	21.6 / 0.91	17.8 / 0.77	25.5 / 1.05	14.3 / 1.05
[DCA]	1-cyanopropyl-3-methylimidaolium	56.0 / 0.22	432 / 1.69	105 / 0.41	41.3 / 0.41
	1-ethyl-3-methylimidazolium	43.4 / 0.39	255 / 2.27	69.6 / 0.63	28.8 / 0.63
[BF ₄]	1-ethanol-3-methylimidazolium	- / 0.10	- / 0.98	- / 0.17	136.1 / 0.17
[PF ₆]	1-ethanol-3-methylimidazolium	- / 0.17	- / 0.77	- / 0.23	59.7 / 0.23

Table 3. Selectivity S_{12}^{∞} and capacity k_1^{∞} values for different separation problems at 323.15 K.

The selectivities for the trihexyl(tetradecyl) phosphonium bis(trifluoromethylsulfonyl)imide are very low compared to the value obtained with imidazolium-based ionic liquids, indicating the limited potential of this phosphonium IL for separation. For instance, the selectivity for hexane/ benzene is 2.2, while it is 60.1 with 1-butyl-3-methylimidazolium tetrafluoroborate or 30.5 with sulfolane used commercially for separating aliphatic/ aromatic hydrocarbons. As observed with imidazolium-based ionic liquids, phosphonium ILs with a long alkyl chain on the cation have a low selectivity. Selectivities obtained with phosphonium or ammonium based ILs are generally of the same magnitude as with classical solvents used in industry. The triethylsulphonium bis(trifluoromethylsulfonyl)imide presents an average values of selectivity and capacity for the aliphatic/aromatic separation problems. (Domańska & Paduszyński, 2010a) found that 1-propyl-1-methylpiperidinium bis((trifluoromethyl)sulfonyl)imide has higher selectivity in the separation of aliphatic from aromatic hydrocarbons than commonly used entrainers. The selectivity is also higher for 1-propyl-1-methylpiperidinium bis((trifluoromethyl)sulfonyl)imide than for 4-methyl-N-butylpyridinium bis((trifluoromethyl)sulfonyl)imide, triethylsulphonium bis((trifluoromethyl)sulfonyl)imide [Et₃S][NTf₂], 1-ethyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [EMIM][NTf₂] and many other ionic liquids with the bis((trifluoromethyl)sulfonyl)imide anion. In the case of bis((trifluoromethyl)sulfonyl)imide anion, the authors found that changing the cation from imidazolium [EMIM]⁺, or sulphonium to piperidinium increases slightly the selectivity and also increases the capacity. Changing the anion from [TF₂N] to [SCN]⁻ increases the selectivity more than three times, but unfortunately decreases the capacity. Selectivities obtained with ammonium based ionic liquid are generally of the same magnitude as with classical solvent used in industry.

7. Conclusion

The increasing interest in ionic liquids leads to more research activities concerning thermodynamic properties of mixtures containing ionic liquids. While data on activity coefficients, VLE and LLE are now available for a number of binary and a few ternary systems, the situation is still not satisfying with respect of a systematic knowledge of these properties and further research work has to fill the remaining gaps. The values of selectivities and capacities obtained for numerous ionic liquids indicate that majority of ionic liquids may replace conventional entrainers applied for the separation processes. These last ten years, few teams around the world demonstrated that the choice of the anion, of the cation but also of the chain influence the efficiency of the ionic liquids to extract a volatile organic compounds. To have a good knowledge on the interactions of ionic liquids with organic compounds, the future work should be focussed on sulphonium, pyrrolidinium, piperidinium based ionic liquids since there is still a lack of data.

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Ionic Liquids (ILs) are one of the most interesting and rapidly developing areas of modern physical chemistry, technologies and engineering. This book, consisting of 29 chapters gathered in 4 sections, reviews in detail and compiles information about some important physical-chemical properties of ILs and new practical approaches. This is the first book of a series of forthcoming publications on this field by this publisher. The first volume covers some aspects of synthesis, isolation, production, modification, the analysis methods and modeling to reveal the structures and properties of some room temperature ILs, as well as their new possible applications. The book will be of help to chemists, physicists, biologists, technologists and other experts in a variety of disciplines, both academic and industrial, as well as to students and PhD students. It may help to promote the progress in ILs development also.

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